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Measurements of quantum yields of bromine atoms in the photolysis of bromoform from 266 to 324 nm

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[1] The quantum yield for the formation of bromine atoms in the photolysis of bromoform, $CHBr_3$, has been measured between 266 and 324 nm. For 303 to 306 nm the quantum yields are unity within the experimental uncertainty of the measurements. At longer wavelengths, where the bromoform cross sections decrease rapidly, an apparent trend to slightly lower quantum yields is probably the result of systematic and random errors or incorrect $CHBr_3$ absorption cross sections. Support for a unit quantum yield for all wavelengths longer than 300 nm comes from the recent theoretical calculations of Peterson and Francisco. At 266 nm the bromine atom quantum yield is 0.76 (±0.03), indicating that at least one additional dissociation channel becomes important at shorter wavelengths. For modeling of the troposphere, it is recommended that a quantum yield of unity be used for wavelengths of 300 nm and longer. *INDEX TERMS:* 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* bromoform, bromine atoms, quantum yield, photolysis

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1. Introduction

[2] Bromoform, $CHBr_3$, is present in the Earth's atmosphere in the parts per trillion (ppt) range [*Berg et al.*, 1984; *Cicerone et al.*, 1988; *Fabian et al.*, 1994; *Sturges et al.*, 2000]. As with other bromonated methanes, the oceans appear to be the major primary source, with secondary contributions from polar microalgae and chlorination of domestic water supplies. Concentrations of bromoform are highest near macroalgae seaweeds, both dissolved in seawater and in the atmosphere [*Moore et al.*, 1993; *Carpenter et al.*, 1999]. A recent estimate of the emissions of organic bromine compounds concludes that the known sources are sufficient to account for the observed atmospheric concentrations [*Carpenter and Liss*, 2000].

[3] Although the concentration of bromine in the stratosphere is much less than that of chlorine, its presence can have a significant effect on ozone destruction because of its longer chain length and the interaction of the bromine and chlorine cycles [*Wofsy et al.*, 1975; *Yung et al.*, 1980; *McElroy et al.*, 1986]. Atmospheric bromine chemistry has been reviewed recently [*Lary*, 1996; *Lary et al.*, 1996].

[4] There has been controversy about the importance of bromoform as a source of bromine in the lower stratosphere. In a survey of the total bromine budget, *Wamsley et al.* [1998] list bromoform under "negligible sources of stratospheric bromine." In contrast, *Dvortsov et al.* [1999, p. 1] concluded that for the midlatitude stratosphere close to the tropopause, "bromoform ($CHBr_3$) alone likely contributes more inorganic bromine than all the conventional long-lived sources (halons and methyl bromide) combined." This view was disputed by the measurements of *Pfeilsticker et al.* [2000] and *Sturges et al.* [2000] and also by the modeling study of *Nielsen and Douglass* [2001]; these studies conclude that the short-lived bromoalkanes (CH_2Br_2, $CHBr_3$, $CHBr_2Cl$) contribute no more than 10 to 30% of the bromine observed in the lower stratosphere.

[5] The atmospheric lifetime of bromoform in the troposphere is approximately a month [*Singh*, 1995; *Butler and Rodriguez*, 1996; *Kurylo et al.*, 1999]. Bromoform is destroyed by photolysis in the near ultraviolet (~75%) and by reaction with OH radicals (~25%). Both processes are thought to eventually release bromine atoms, but the mechanism and the efficiency of these releases have not

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been determined. This paper reports laboratory measurements of bromine atom formation for $CHBr_3$ photolysis in the near ultraviolet.

2. Description of Experiments

[6] The photolysis of $CHBr_3$ was studied in a square (5 × 5 cm) aluminum tube 26 cm long, equipped with Brewster angle windows at both ends. The gas flow entered near the front window and exited near the rear window. A YAG laser (Continuum PL8000) provided pulsed radiation at 266 nm with a beam diameter of 5 mm. The YAG was also used at 532 nm to pump a dye laser (PDL-3) using various dyes (Rhodamine 640, Sulforhodamine 640, DCM). The red output from the dye laser was doubled to give radiation in the range 303 to 324 nm. The doubled dye laser pulses were expanded by a factor of three before entering the photolysis cell, giving them a diameter of about 5 mm. Both beams traversed the center of the photolysis cell. A joule meter (Molectron EPM 1000) measured the average pulse energy at the front window just before and just after each photolysis run, and the average of the two measurements was used in the quantum yield determinations. While the doubled dye laser pulses passed through the Brewster window with no reflection loss, the 266 nm radiation had the wrong polarization, and so a correction was needed for the reflected radiation (measured as 4.5%).

[7] Bromine atoms were measured by vacuum ultraviolet resonance fluorescence with a combination of emission lines between 130 and 163 nm. A sealed lamp with MgF_2 window was excited by a ~10 watt, 180 MHz radio-frequency discharge and the emission was stabilized by an active feedback loop that maintained a constant IR output at ~840 nm [*Toohey et al.*, 1987; *Brune et al.*, 1989; *McKinney et al.*, 1997]. A solar blind photomultiplier (PM) with potassium bromide photochathode (EMR Model 541J) observed the scattered resonance lines at right angles to both the gas flow and the Br lamp radiation. Razor blade light traps on the walls opposite both lamp and detector served to reduce scatter off surfaces. TTL pulses (<60 ns full width, half maximum) from an amplifier discriminator (Research Support Instruments) were counted as a function of time on a multichannel scaler (Ortec MCS-pci), stored and analyzed by weighted least squares using the PSI-Plot program.

[8] Bromoform was introduced by bubbling nitrogen or air at atmospheric pressure through liquid $CHBr_3$ at a temperature of 13 to 17°C. Most of the flow entered the vacuum system through a flow controller, while the excess mixture flowed through a 10 cm cell in a spectrophotometer (Cary model 4E). By continuously monitoring the absorbance at 266 nm, the concentration of $CHBr_3$ could be averaged over the course of a photolysis run. For the experiments using a mixture of molecular chlorine and vinyl bromide instead of bromoform, a similar procedure was used for monitoring Cl_2 using its absorbance at 330 nm. A separate spectrum of pure vinyl bromide showed that its cross section at 330 nm was 10^3 times less than that of Cl_2 and so for the concentrations used, vinyl bromide did not interfere with the Cl_2 measurements. Typical concentrations of the active ingredients are given in the caption to Figure 1.

[9] The pressure in the photolysis cell was varied from 1.5 to 20 Torr with no significant effect on the yield of bromine atoms. The quantum yield measurements were done at total pressures of 2 and 10 Torr and with a pulse repetition rate of 10 Hz. For the flow rates used and this pulse rate, each parcel of gas was exposed to three laser pulses. No difference in bromine atom yield was observed when the pulse repetition rate was varied between 10 Hz and 0.1 Hz. For the conditions used in the quantum yield experiments, the two spin states of the bromine atoms ($^2P_{3/2}$ and $^2P_{1/2}$) should have reached their equilibrium ratio within a millisecond. To be sure that this was not a problem, some runs used a mixture of 5% H_2 in N_2 as the carrier gas to increase the relaxation rate by a factor of ten [*Johnson et al.*, 1996]; there were no detectable differences in the yields or time dependence of Br signals when H_2 was present. The bromine atom signals increased linearly with pulse energy up to well above 1 mJ per pulse; quantum yield measurements were made with pulse energies of 0.8 to 1.2 mJ per pulse.

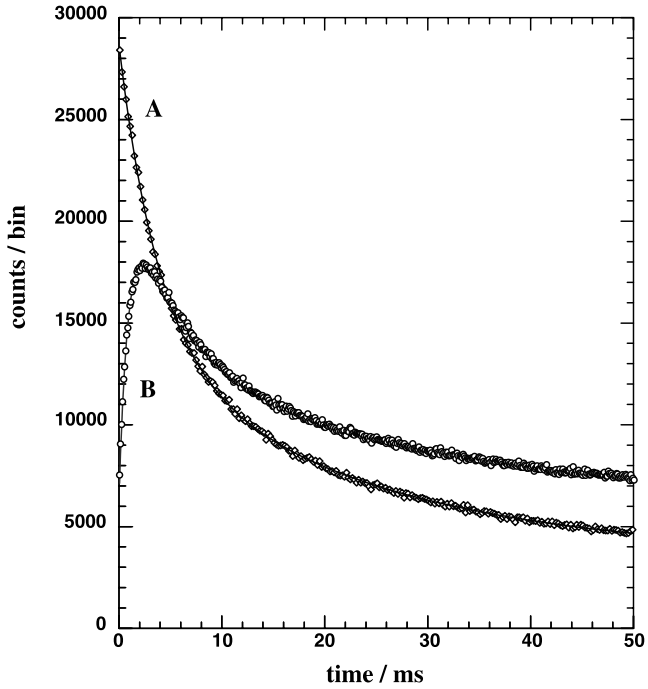

Figure 1. Examples of signals using method I (A) and method II (B). For trace A: $[CHBr_3] = 3.94\ 10^{13}$ molecules cm^{-3}; balance N_2; total pressure 2.04 Torr; laser at 266 nm, 0.96 mJ $pulse^{-1}$; 0.2 ms bin^{-1}, 3000 sweeps added. For trace B: $[Cl_2] = 2.6\ 10^{13}$ molecules cm^{-3}; $[C_2H_3Br] = 6.0\ 10^{12}$ molecules cm^{-3}; balance N_2; total pressure 2.04 Torr; laser at 305 nm, 1.18 mJ $pulse^{-1}$; 0.1 ms bin^{-1}, 2000 sweeps added.

[10] The temperature of the gas in the photolysis cell was slightly above room temperature due to heating of the walls of the flow tube by the resonance lamp. A thermocouple at the center of the tube just downstream from the detection region registered 31°C. This temperature was used to calculate the bromoform and chlorine cross sections [*DeMore et al.*, 1997]. The bromoform (Aldrich Chemical 99 + %) was analyzed by gas chromatography; no CBr_4 was evident and only a trace of CH_2Br_2 (<0.1%) could be detected. The chlorine/vinyl bromide mixture was made

from neat vinyl bromide (Aldrich Chemical 98%) and a 1% Cl_2 in helium mixture (Matheson) and was stored in a 5 liter bulb in the dark.

3. Experimental Results

[11] Two methods were used to measure the quantum yields of Br atoms from $CHBr_3$. Method I compared the amplitude of the Br signal when using the doubled radiation from the dye laser (303 to 324 nm) to that when using 266 nm radiation directly from the YAG laser. This method had the advantage of being able to switch the wavelength easily without disturbing the gas flow; the bromoform concentration was relatively stable throughout the day, affected only by a slight drift to higher values as the bath surrounding the bubbler warmed slightly. Since the identical gas mixture was used during both measurements, no correction for absorption of the bromine resonance lines by the $CHBr_3$ within the photolysis cell was needed.

[12] In method I, the bromine atom resonance fluorescence signals as a function of time, t, were fit to the equation,

$$\text{Signal} = S_0(\exp(-K_1\ t)) + S_1(\exp(-K_2\ t) - \exp(-K_1\ t)) + Bk \quad (1)$$

This double exponential decay was necessary for runs at all pressures. The decay constants K_1 and K_2 were inversely proportional to total pressure, indicating diffusion controlled losses. The faster loss process ($K_1 = 250\ s^{-1}$ at 2 Torr) was interpreted as diffusion of bromine atoms out of the most sensitive detection region, and the slower process ($K_2 = 40\ s^{-1}$ at 2 Torr) was probably loss of bromine atoms on the walls of the flow tube. S_0 is the amplitude of the bromine atom signal at t = 0, and this was used as the measure of the number of Br atoms formed by the laser. S_1 was typically 45% as large as S_0. The term Bk represents the background count, which contained contributions from scattered light, as well as a time-independent signal from the presence of bromoform within the flow tube. Trace A in Figure 1 shows a typical signal observed using method I together with the least squares fit to equation (1).

[13] For experiments at 320 and 324 nm, the Br signals were quite weak. For these experiments, values for K_1, K_2, and the ratio S_1/S_0 from 266 nm runs, which had strong signals, were inserted into equation (1), and then the least squares fits were used to determine S_0 and Bk. Normally values for K_1, K_2 and S_1/S_0 were constant to within a few percent on any given day, as long as the flow conditions remained constant.

[14] After normalizing the signal amplitudes, S_0, for slight differences in bromoform concentration (as measured by absorbance in the Cary), pressure within the photolysis cell, and laser pulse energy multiplied by wavelength (to convert energy to number of photons), the ratio of normalized signals gave the ratio of products of cross section (σ) times quantum yield (ϕ) at the two wavelengths:

$$\frac{\mathbf{S}_o(\lambda)}{\mathbf{S}_o(266)} = \frac{\boldsymbol{\sigma}_\lambda \phi_\lambda}{\boldsymbol{\sigma}_{266}\phi_{266}}$$

Literature values for the absorption cross sections of bromoform were then used to calculate the ratio of quantum yields at the two wavelengths [*Gillotay et al.*, 1989; *Moortgat et al.*, 1993]. The results obtained using method I are collected in Table 1.

Table 1. Experimental Results Using Method I[a]

λ, nm	Carrier	σ_λ	$\varphi_\lambda/\varphi_{266}$	95% C.L.	N	φ_λ	Estimated Error
303.0	N_2	0.501	1.323	0.65%	5	1.009	6.3%
306.0	N_2	0.329	1.216	2.7%	6	0.927	6.9%
306.0	air	0.329	1.183	3.7%	6	0.902	7.3%
310.0	N_2	0.188	1.181	1.0%	5	0.901	6.4%
314.0	air	0.1073	1.188	5.1%	6	0.906	8.2%
314.0	N_2	0.1073	1.158	10.0%	4	0.883	11.9%
320.0	air	0.0463	1.060	12.6%	6	0.809	14.2%
320.0	N_2	0.0463	1.086	8.7%	6	0.828	10.9%
324.4	N_2	0.0250	1.000	33%	3	0.762	34%

[a]The cross sections σ_λ are calculated for bromoform at 31°C; units are 10^{-20} cm^2. N is the number of measurements that have been averaged for each condition. Values of φ_λ are calculated from the ratios $\varphi_\lambda/\varphi_{266}$ by using $\varphi_{266} = 0.763$ from method II (see Table 2).

[15] Method II compared the bromine atom signals for two different gas mixtures at the same photolysis wavelength. One gas mixture was the same $CHBr_3/N_2$ mixture that was used in method I. The other gas mixture contained molecular chlorine and vinyl bromide diluted with nitrogen. The laser pulse dissociated the molecular chlorine and the chlorine atoms were rapidly converted to bromine atoms by reaction with vinyl bromide [*Park et al.*, 1983]:

$$\begin{aligned}
Cl_2 + h\nu &\longrightarrow 2\ Cl \\
Cl + CH_2CHBr &\longrightarrow Br + CH_2CHCl \qquad k_1 \\
Cl &\longrightarrow \text{loss by diffusion} \qquad k_2 \\
Br &\longrightarrow \text{loss by diffusion} \qquad k_3
\end{aligned}$$

There was no evidence of photolysis of the vinyl bromide; no time-dependent Br signals appeared unless both Cl_2 and CH_2CHBr were present.

[16] The time dependence of the resonance fluorescence signals for the Cl_2/C_2H_3Br mixtures was different from that observed with bromoform. As shown in trace B in Figure 1, the signal increases rapidly after the flash, as Cl atoms are converted into Br atoms, and then decays with the same double exponential decay observed for bromoform. For these mixtures, the signals could be fit to an equation of the form,

$$\begin{aligned}\text{Signal} = {} & S_0(\exp(-K_1\ t) - \exp(-K_0\ t)) \\ & + S_1(\exp(-K_2\ t) - \exp(-K_1\ t)) + Bk \end{aligned} \quad (2)$$

where K_0 is the rise-time constant and K_1 and K_2 are again the two decay constants.

[17] The mechanism used to model this time dependence was as follows. The chlorine atoms are formed by the laser pulse with a concentration $[Cl]_0$. Chlorine atoms are removed by reaction with vinyl bromide, with a rate constant k_1, or they can diffuse out of the viewing region with a decay constant k_2; for simplicity, only a single diffusional decay will be used here. The bromine atoms are removed only by diffusion, with a rate constant k_3. Solving the resulting differential equations, with the boundary condition that [Br] = 0 at t = 0, gives the following expression for the bromine atom concentration,

$$\begin{aligned}[Br] = {} & [Cl]_0\{k_1[VB]/(k_1[VB] + k_2 - k_3)\} \\ & \cdot \{\exp(-k_3\ t) - \exp(-(k_1[VB] + k_2)t)\}\end{aligned}$$

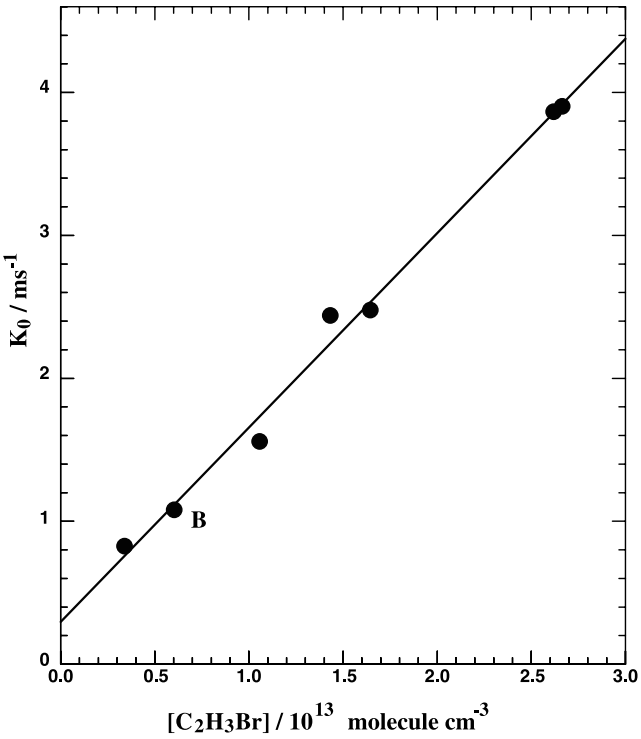

Figure 2. The rise time constant, K_0, as a function of the vinyl bromide concentration. The point marked B is from trace B in Figure 1. Except for the varying $[C_2H_3Br]$, the conditions are similar to those described for trace B.

where [VB] is the vinyl bromide concentration and the rate constants are defined above. Comparing this expression to the first term in the empirical fitted equation (2), it can be seen that the time constants are,

$$K_0 = k_1[VB] + k_2$$
$$K_1 = k_3$$

and the fitted amplitude S_0 can be written as,

$$S_0 = [Cl]_o\{(K_0 - k_2)/(K_0 - k_3)\}$$

[18] As required by the above model, the rise time constant K_0 was observed to depend linearly on the vinyl bromide concentration, as shown in Figure 2. The slope of the least squares line in Figure 2 gives a value for k_1, 1.36×10^{-10} cm^3 $molecules^{-1}$ s^{-1}, that agrees very well with the only previous measurement (1.43×10^{-10}) by *Park et al.* [1983]. The intercept in Figure 2 gives a value for k_2 of 295 s^{-1}.

[19] Several corrections were needed when calculating quantum yields by method II. The most important correction was an allowance for the attenuation of the Br resonance radiation during its approximately 5 cm path through the two different gas mixtures. In separate experiments, measurements of the amplitude of the normalized signal as a function of $CHBr_3$ or Cl_2/VB mix concentrations within the flow cell resulted in reasonable Beer's Law plots. The slopes of these plots were used to calculate cross sections of $\sim 1.1 \times 10^{-16}$ cm^2 $molecule^{-1}$ for $CHBr_3$ and $\sim 2.1 \times 10^{-16}$ for the Cl_2/VB mixture. Since the bromine resonance lines occur at several wavelengths, these are only effective cross sections, but they are consistent with what is known about the absorption spectra of $CHBr_3$ and Cl_2 near 160 nm [*Henrici*, 1932; *Lee and Walsh*, 1959]. These Beer's Law slopes were then used to correct the measured S_0's in the quantum yield measurements; these corrections were +2 to 3% for $CHBr_3$ and +11 to 12% for Cl_2/VB.

[20] A second adjustment was needed for the Cl_2/VB experiments to correct the amplitude of the signal so that it was proportional to the original chlorine atom concentration. This involved multiplying S_0 for each run by the factor $(K_0 - k_3)/(K_0 - k_2)$, where k_2 is the intercept in Figure 2 and k_3, the diffusional loss rate constant for Br atoms, was taken to be the fitted value of K_1 in equation (2). Since values of K_0 were 1000 to 4000 s^{-1} and the fitted k_3 ($\sim$240 s^{-1}) were only slightly smaller than k_2 (295 s^{-1}), these corrections were in the range of 2 to 8%.

[21] With the amplitudes normalized for slight drifts in concentration, pressure and laser intensity as in method I, the ratio of corrected S_0 were taken to be the ratio of the product of the quantum yield and cross section for the two absorbers, $CHBr_3$ and Cl_2. The quantum yield of Cl_2 is assumed to be 2.0 and so the quantum yield of $CHBr_3$ could be calculated. The results of method II are summarized in Table 2. The $CHBr_3$ quantum yields from both methods I and II are plotted as a function of wavelength in Figure 3.

[22] When N duplicate runs were averaged, the sample standard deviation was used with Student's t distribution and (N-1) degrees of freedom to set 95% confidence limits on the reported mean values. These confidence limits, based only on the scatter of the data, are given in Tables 1 and 2. There were additional errors that could only be estimated: using the dye laser, there was an estimated wavelength uncertainty of 0.3 nm, which resulted in an uncertainty of about 4% in the cross sections; a temperature uncertainty of 2 K gave uncertainties in the cross sections of 1.5 to 2.5%; and for method I, the estimated uncertainty of 4.4% in the quantum yield of $CHBr_3$ at 266 nm contributed to the uncertainty reported at other wavelengths. These estimated uncertainties were combined with the 95% confidence limits to give the total uncertainties listed in the last columns of Tables 1 and 2.

4. Discussion

[23] It is not surprising that the quantum yield of bromine atoms in Figure 3 is unity or close to unity in the 300 nm region. The bromoform spectrum is an absorption continuum with a maximum near 220 nm and a long tail extending out to at least 360 nm [*Moortgat et al.*, 1993]. Such extended continua are common features of halogenated alkanes and they are usually interpreted as transitions to a

Table 2. Experimental Results Using Method II[a]

λ, nm	σ_{CHBr3}	σ_{Cl2}	$\varphi_{CHBr3}/\varphi_{Cl2}$	95% C.L.	N	φ_{CHBr3}	Estimated Error
266.0	48.3	0.496	0.381	2.8%	3	0.763	4.4%
303.0	0.501	13.9	0.470	3.6%	5	0.939	6.9%
305.0	0.379	15.2	0.512	11.5%	7	1.025	12.9%
306.0	0.329	15.9	0.513	5.9%	3	1.026	8.0%

[a]The cross sections, σ, are calculated for 31°C; units are 10^{-20} cm^2. The quantum yield of chlorine atoms from Cl_2, φ_{Cl2}, is assumed to be 2.

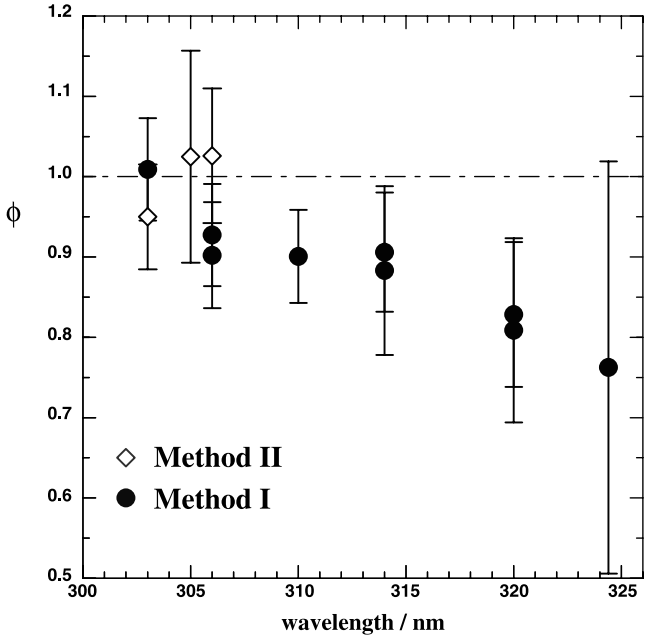

Figure 3. The quantum yields of bromine atoms from bromoform as a function of wavelength. Values for method I come from Table 1. Values for method II come from Table 2. Trace B of Figure 1 is one of the seven runs contributing to the point at 305 nm. The error limits come from the last columns of Tables 1 and 2.

repulsive state that correlates with the separated ground state halogen atom and an alkyl radical [*Herzberg*, 1966]. The smooth decrease in absorption cross section to longer wavelengths is interpreted as a decreasing Franck-Condon overlap between the ground vibrational state and the repulsive upper state potential energy curve [*Gordus and Bernstein*, 1954].

[24] However, there are other dissociation processes that are energetically accessible in this wavelength region. In addition to the expected single bond rupture, A, three other channels are energetically possible, B, C and D:

Channel A	$CHBr_3 + h\nu \longrightarrow Br + CHBr_2$	$\lambda < 435$ nm
Channel B	$CHBr_3 + h\nu \longrightarrow HBr + CBr_2$	$\lambda < 410$ nm
Channel C	$CHBr_3 + h\nu \longrightarrow Br_2 + CHBr$	$\lambda < 337$ nm
Channel D	$CHBr_3 + h\nu \longrightarrow H + CBr_3$	$\lambda < 304$ nm
Channel E	$CHBr_3 + h\nu \longrightarrow 2\ Br + CHBr$	$\lambda < 207$ nm

The formation of two bromine atoms from the absorption of one photon, channel E, is clearly not possible for the current experiments. The above wavelength limits were calculated using standard heats of formation together with calculated values for CHBr and CBr_2 [*Dixon et al.*, 2002; *Xu et al.*, 2002].

[25] Both method II and method I (using the method II quantum yield at 266 nm) agree that the bromine atom quantum yields at 303 to 306 nm are unity within the experimental error. Thus only channel A can be active in this region. This finding is supported by the theoretical calculations of *Peterson and Francisco* [2002], who find that the only electronically excited state of $CHBr_3$ accessible at wavelengths longer than 270 nm is an unstable triplet state that is dissociative along the C-Br coordinate.

[26] Is the apparent decrease in quantum yield at wavelengths longer than 300 nm (Figure 3) the result of channels B and C becoming important? Mechanistically this seems unlikely. With a repulsive upper state, the longer the wavelength the longer is the carbon-bromine bond in the newly formed electronically excited molecule. This greater distance would make it harder for the departing Br atom to capture an H or another Br, channels B or C. Fluorescence of the electronically excited $CHBr_3$ would also decrease the bromine atom quantum yield, but this is a very inefficient process for a repulsive state.

[27] It is more likely that the bromine atom quantum yield remains at unity, and the apparent decrease at longer wavelengths observed in Table 1 and Figure 3 is due to random or systematic errors that become more prominent as the cross sections decrease. Certainly at 324 nm, the random errors dominate; for an integration time three times longer than that used at shorter wavelengths, the amplitude of the Br signal was only 350 counts/bin, while the background count was 35,000 counts/bin. The longer counting times also increased the error due to lamp drift. In addition, the quantum yields are fully dependent on the bromoform cross sections reported by *Moortgat et al.* [1993]. The cross sections at the longer wavelengths would have to be too large by 10 to 20% to return the long wavelength experimental points in Figure 3 to unity. However, *Moortgat et al.* [1993] claim that their cross section errors are only about ±3% in this region; this 3% uncertainty has not been included in the error bars shown in Figure 3.

[28] More surprising is the bromine atom quantum yield of 0.76 at 266 nm. This suggests that at least one of the channels B, C or D becomes important at this shorter wavelength. The molecular beam time-of-flight studies of *Xu et al.* [2002] report evidence that both channels A and C are important in the 200 nm region. They estimate that the Br_2 yield, resulting from channel C, is 0.16 at 267 nm and 0.26 at 234 nm. At these higher energies there is more chance of mixing with other electronic states having different properties and so additional dissociation processes occur. We believe that the more quantitative determination of the bromine atom quantum yield of 0.76 at 266 nm is to be preferred over the estimate of 0.84 of *Xu et al.* [2002].

[29] For modeling the bromine budget in the troposphere, where the radiation is mostly at wavelengths longer than 300 nm, it is recommended that a quantum yield of unity be used for channel A. In the atmosphere, the dibromomethyl radical that is also formed in channel A should rapidly form a peroxy radical, $CHBr_2O_2$. The fate of this peroxy radical has been investigated by *Orlando et al.* [1996].

[30] In the stratosphere, as more radiation shorter than 300 nm becomes available, the photochemistry of bromoform will become more complicated. However, measurements of $CHBr_3$ in the stratosphere [*Sturges et al.*, 2000] show that its concentrations plunge rapidly with height above the tropopause, so that the importance of bromoform as a direct source of bromine atoms in the stratosphere is probably minor.

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